

Effect of albumin content on the rheological properties and wet foam stability of porous ceramics

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The stabilization of wet foam was an important parameter for obtaining a large volume of dried foam in SiC porous ceramics. Octylamine was used as a foam stabilizer, which modifies the particle surface. Albumin was added as a foaming agent to achieve a higher volume of wet foam with higher stability. Viscosity of the colloidal suspension varying with albumin content was found to be typical, as on increasing albumin content, the slurry showed shear thickening behavior. The viscosity of the slurry was found to be increased, hindering thick strutting. This gave more stability to the wet foam on mechanical frothing, to produce porous ceramics on sintering. In terms of the rheological properties, wet foams were characterized as a function of air content, wet foam stability, bubble size, and relative bubble size. Controlling the air content inside the foam, the wet foam stability of the wet foams was improved from 20 to 90% with the increment of albumin content. Proof of the stability is shown by the controlled increment of the relative bubble size to less than 2.5 times. With all these improved parameters upon sintering, highly interconnected pore structure was achieved for various applications.

Key words: SiC, Rheological properties, Foaming agent, Wet foam, Porous ceramics.

Introduction

Porous ceramics refers to a high-temperature firing. The inner parts have massively connected to each other, or close to the pores of the ceramic material. Porous ceramic development began in the 1870s when it was initially used as a bacterial filter material. But its excellent performance has resulted in porous ceramics being gradually used in the fields of metallurgy, chemical sector, environmental protection, energy, and biological aspects [1, 2]. The uniform permeability of porous ceramic can be applied to a variety of filters, separation devices, and can even produce a fluid distribution component, mixing elements and exudative components [3, 4]. Porous ceramic with developed surface area can produce a variety of porous electrode, catalyst carrier, and can even be used in heat exchangers, gas sensors, and other fields. Porous ceramics can also be used for a variety of insulation materials, and lightweight structural materials. Coupled with its high temperature and corrosion resistance, it has aroused great attention globally in material science and has been developing rapidly [5].

SiC ceramics are important in a variety of industrial applications, due to their unique properties, such as excellent compressive strength of (450-520) kg/mm²,

with high fracture toughness (4.6 MN/m^{3/2}), good chemical resistance, high thermal conductivity (146 WmK), moderate thermal expansion coefficient (4×10^{-6} /°C), and high thermal shock resistance [6-8]. Hence these properties make porous SiC ceramics applicable for catalytic supports, separation membranes, acoustic and thermal insulators, liquid gas filters, high-temperature structural materials, high-temperature/high-voltage semiconductor electronics, and reinforcement of composites [9, 10]. Different processing routes exist for porous ceramics, and direct foaming is particularly suitable to fabricate porous structures with a pore size of between 30 mm and 1 mm³ [11, 12]. Simplicity, environmental friendliness, and low production cost make direct foaming particularly interesting for industrial manufacturing [13, 14].

Direct foaming involves the production of a porous material through direct incorporation of air into a suspension or liquid media via mechanical frothing, generating air bubbles inside the ceramic suspension. Here, the bubbles are incorporated in the wet state that must be set, and in most cases, the foam must also be sintered, either in a gaseous medium or in a vacuum, to maintain the pore structure [15-17]. Addition of surfactant can reduce the surface tension, which affects the surface viscosity, preventing a collapse in the suspension through electrostatic force. The pH, rheological effect, and colloidal properties influence the stability of the colloidal suspension [18-20].

This study investigates the stability of the suspension

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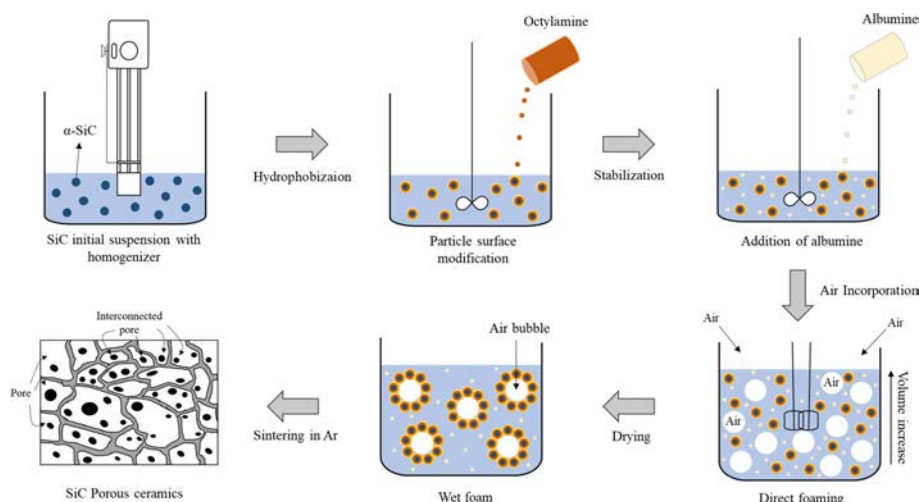


Fig. 1. Schematic diagram of the direct foaming technique of SiC porous ceramics.

as a function of various parameters. The viscosity of the slurry varying with the albumin content was found to be typical, as on increasing the wt.% of albumin content, the slurry showed shear thickening behavior. The increased viscosity of the slurry was found to hinder thick strutting, to provide more stability of the wet foam on mechanical frothing. On sintering, this gave a porous ceramics. In terms of the rheological properties, wet foam was characterized as a function of air content, wet foam stability, bubble size, and relative bubble size. Controlling the air content inside the foam improved the wet foam stability of the wet foam from 20 to 90% with the increment of albumin content. Proof of the stability was shown by the controlled increment of the relative bubble size to less than 2.5 times. With all these improved parameters upon sintering, a highly porous open pore ceramics was achieved for various applications.

Experimental Procedure

Materials

The particles that were used in the experiments were SiC powder (0.4 μm , USA) with a mean particle diameter (d_{50}) of 0.4 μm , and a density of 3.17 g/cm^3 . The other chemicals were Octylamine (98%, Wako Pure Chemical Industries, Japan) that was used as a surfactant, and hydrochloric acid (35%, Yakuri Pure Chemicals, Osaka, Japan) and sodium-hydroxide (Yakuri Pure Chemicals, Kyoto, Japan) that were added to control the pH of the suspension. Albumin (Daejung, South Korea) was used as a foaming agent to provide stability of the colloidal suspension for the tailoring of open, interconnected highly porous ceramics.

Preparation of suspension

The SiC powder (d_{50} ~0.4 μm ; Sika Densitac, Saint Gobain, France) was added to de-ionized water, and

was homogeneously mixed with the help of homogenizer HM1200D, LAB STIRRER, 142K, Korea). Homogenization and de-agglomeration of the suspension was carried out by mixing the suspension in a homogenizer for 30 min with the speed of 4,000 rpm. After homogenizing the initial suspension, 12.5 wt.% of Octylamine (98%, Wako Pure Chemical Industries, Japan) was added to the SiC suspension as a surface modifier, to partially hydrophobize the surfaces of the SiC particles, then albumin (Daejung, South Korea) of different concentration from up to 12.5 wt.% was added to the suspension as a foaming agent. The pH of the suspension was adjusted to 10 by adding (4) M NaOH and/or (10) N HCl (Yakuri Pure Chemicals, Japan), dropwise. Through the addition of the required amount of water, the solid content of the final aqueous suspension was set to 23.8 vol.%. Under a 40 min observation, the final suspension was then instantly foamed using mechanical frothing, as shown in Fig. 1.

Rheological properties

The rheological behavior of all the studied slurry was determined by rheometer (MCR502, Anton Paar, Germany) with a cone-cup type (CC 27, cone diameter 27 mm) at temperature 25 $^{\circ}\text{C}$ for the SiC slurry, and double gap type (DG26.7, cup diameter 26.7 mm) for albumin, which has relatively low viscosity. The flow curves of the slurries were measured for shear rates from (1 to 1,000) /s with variable duration from (10 to 1) s for an overall 120 s.

Colloidal suspension & foam characterization:

The air content was calculated as the increment in the volume of the suspension after foaming in percentage, as follows:

$$\text{Air content} = \frac{(V_{\text{wet foam}} - V_{\text{suspension}}) \times 100\%}{V_{\text{wet foam}}} \quad (1)$$

where, $V_{\text{wet foam}}$ indicates the volume of wet-foam volume after foaming, and $V_{\text{suspension}}$ indicates the pre-foaming suspension volume.

To investigate the wet-foam stability, the wet-foam samples were filled into cylindrical molds of constant volume and left for 48 h. The foam stability was then evaluated upon the observation of the decrement in the volume of the foam in percentage, as follows:

$$\text{Wet foam stability} = \frac{R_{\text{curing time}}}{R_{\text{Initial}}} \quad (2)$$

where, V_{Final} indicates the wet-foam volume after the 48 h, and V_{Initial} indicates the wet-foam volume before the 48 h.

The bubble size and distribution of the colloidal suspension after mixing for 40 min was evaluated using a digital camera, and the linear intercepts were measured by optical microscopy in transmission mode (Somtech Vision, South Korea).

The relative bubble size was measured by calculation of the percentage of the volume increase of the suspension post-foaming, as follows:

$$\text{Relative bubble size} = \frac{R_{\text{curing time}}}{R_{\text{Initial}}} \quad (3)$$

where, R_{initial} indicates the radius of the initial bubble of the colloidal suspension, and $R_{\text{curing time}}$ indicates the radius of bubble after curing of the colloidal suspension for a certain period of time.

Drying, sintering, and analysis

The wet foams were filled into cylindrical molds and left to dry at room temperature of (22 to 25) °C for (24 to 48) h. After drying at room temperature, the specimens were sintered at 2,150 °C for 1 h in Ar medium. The heating and cooling rates were set to (1 and 3) °C/min, respectively. The microstructures of the sintered foams were observed by field-emission scanning electron microscopy (FESEM) (JEOL, Japan).

Results and Discussion

Fig. 2 shows the flow curves of the SiC slurry with different amount of albumin content. The viscosity of SiC slurry without albumin was taken to check the viscosity of the original suspension, and to compare with SiC slurry with albumin. The viscosity of the SiC slurry increases as the albumin content increased, and the viscosity of the colloidal suspension decreases as the albumin is added to the colloidal suspension, with an increase in shear rate. Fig. 2 illustrates that all suspensions exhibit a typical shear-thinning behavior, and this is attributed to the large effect of the Van der Waals forces. Van der Waals forces are always present in a colloidal system [23], and the addition of albumin leads to a considerable increase in viscosity.

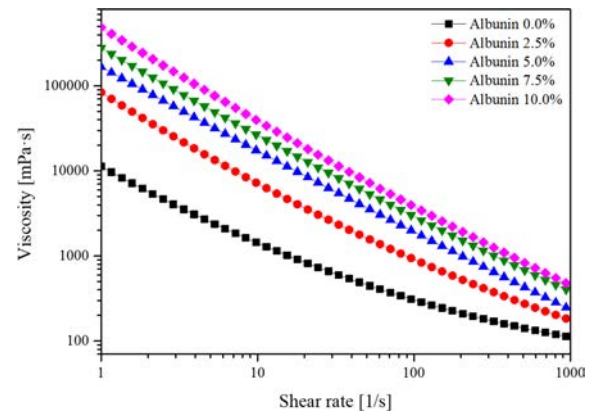


Fig. 2. Viscosity and shear rate of the colloidal suspension with respect to the different wt.% of albumin content.

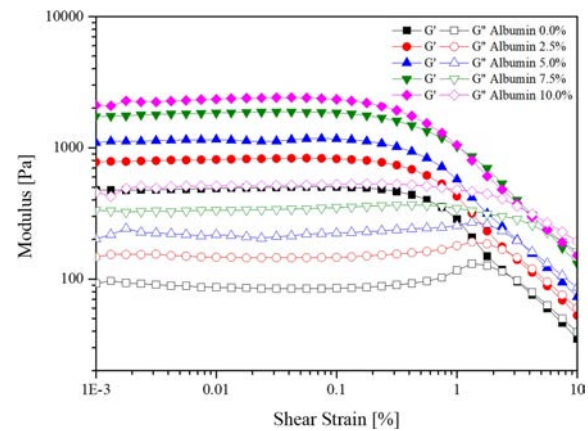


Fig. 3. Oscillation mode amplitude sweep of the slurry with respect to the albumin content.

Fig. 3 shows the storage and loss modulus analyzed with a difference in the shear strain, with an amplitude sweep measurement in the oscillation mode. The amplitude sweep of the strain vs modulus, the section for the linear storage modulus (G'), LVE range, and limiting value of the LVE range are designated where the storage modulus begins to decrease. The limiting shear strain of 0.02% was fixed to compare the frequency sweep of the slurries. The storage modulus (G') was measured to be linear and to decrease at the shear strain due to material's internal structure breaks. The storage modulus (G') and the loss modulus (G'') cross where flow begins, which increases as the albumin content increases. The graph shows that the colloidal suspension with more than 5 wt. % albumin forms a viscoelastic gel with a high gel strength that shows the strongest resistant to permanent deformation (yielding) under applied stress condition.

Fig. 4 shows the 3ITT flow curve of the albumin content with Interval 1 (shear rate 1 s⁻¹, 15 s)-Interval 2 (shear rate 500 s⁻¹, 10 s)-Interval 3 (shear rate 1 s⁻¹, 60 s). As a typical result, the interval 1 and interval 3 flow curves are presented using linear scales. The analysis for Interval 3 shows in which time which percentage of

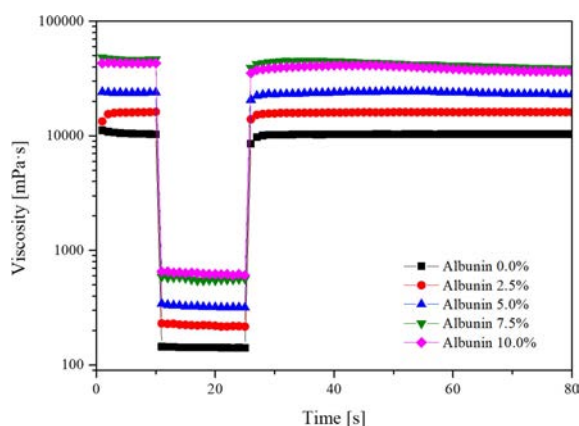


Fig. 4. 3ITT flow curve of albumin contents with the different shear rate at a different interval.

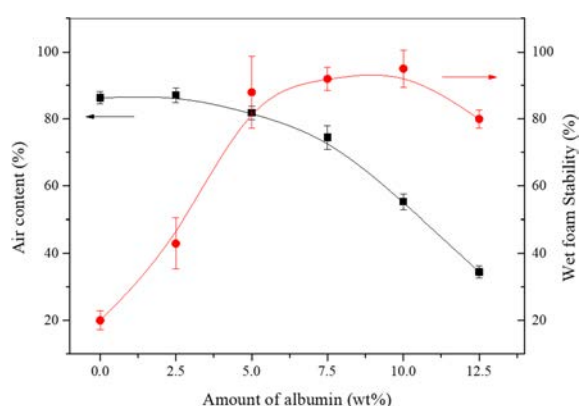


Fig. 5. Air content and wet foam stability with respect to the albumin content.

the structure recovery takes place within a certain time period (compared to interval 1) [19, 20]. The recovery is higher when the albumin content is added of interval 2. However, when the amount of albumin exceeded 7.5%, recovery was lowered. The recovery is within 1 sec for the slurry with 7.5 wt.% albumin, and the viscosity in Interval 1 increased higher than the viscosity in Interval 3. The slurry with 7.5 wt.% albumin revealed a higher thixotropy than the slurry with 0% albumin, and the recovery is 99% when the shear rate for interval 2 is 500 s^{-1} . This higher thixotropy results in a better colloidal suspension for the stable wet foam.

Fig. 5 shows the air content and average wet foam stability of the SiC suspension with respect to the albumin contents. High-volume foams with an air content of up to 84% were formed upon the mechanical frothing, which strongly indicates the stabilization of the wet foam, due to the attachment of the particles at the air/water interface. The wet foam stability and the air content were measured in term of albumin contents. It is evident that with the albumin content increment up to 5.0 wt.%, the air content was slightly decreased whereas the wet foam stability was increased. With the

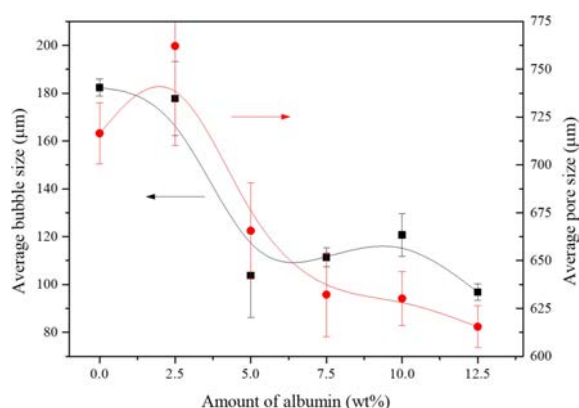


Fig. 6. Average bubble size with respect to the albumin content.

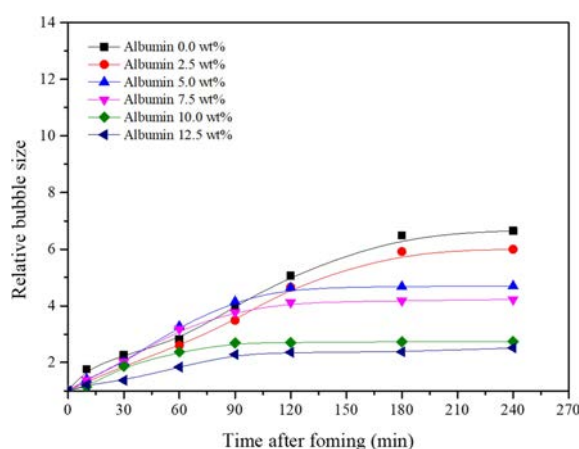


Fig. 7. Relative bubble size of SiC suspension having different albumin concentrations with respect to the amount of time after direct foaming.

increasing the albumin from 5.0 to 12.5 wt.%, the air content was vigorously decreased but wet-foam stability was increased to 87 and 90%, respectively. The maximum wet foam stability with the higher air content was found at 10 wt.% of albumin content.

Fig. 6 shows the average bubble size of the SiC suspension, and also the pore size of the SiC porous ceramics with respect to the albumin content. High-volume foams with air content up to 84% form upon the occurrence of mechanical frothing as shown in Fig. 6, which strongly indicates the stabilization of air bubbles, due to the attachment of the particles to the air/water interface. The decrease of bubble size with the increase of albumin content is related to the densification of porous ceramics, and the albumin is considered to affect densification. Also, it is affected by the decrease of the average bubble size and the influence of the change of the relative bubble size and the microstructure. As the pore size of the sintered sample was larger than the wet foam state having from 200 to 120 μm with the addition of albumin in the range of 2.0 to 5.0 wt.%, respectively. This increment in the pore size can be attributed to the Ostwald

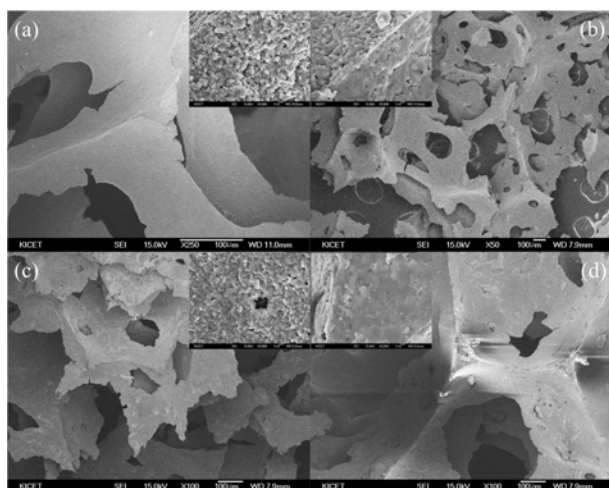


Fig. 8. FESEM images of the porous SiC ceramics sintered at 2,150 °C for 1 h with the albumin contents of (a) 2.5, (b) 5.0, (c) 7.5, and (d) 10.0 wt.%.

ripening defect, which leads to the steady growth in the bubble size giving unstable wet foam during the drying process [13], as shown in Fig. 7.

Fig. 7 shows the relative-bubble-size time with drying time of 240 min, where the bubbles tended to collapse after 1 h due to the effect of the Ostwald-ripening destabilization mechanism that leads to the steady growth of the bubble size, thereby resulting in an unstable wet foam. The SiC colloidal suspension without the albumin shows the maximum relative increase of the bubble size after 2 h. The bubbles with the albumin contents of 2.5 and 5.0 wt.% exhibited higher increments of relative bubble size with respect to the albumin contents of 7.5 and 10.0 wt.%, whereas the albumin contents of 7.5 and 10.0 wt.% are considerable, with a nearly constant relative bubble size, respectively. Also, for the corresponding solids loading and albumin content, a minimum pressure difference between the bubbles of different sizes is necessary to ensure the stability of the foam, and to overcome defects, such as coalescence and drainage. The experimental values also provide the reason for the pore-size increment that occurred upon the application of the sintering.

Fig. 8 shows the microstructure of porous ceramics with respect to (a) 2.5, (b) 5.0, (c) 7.5, and (d) 10.0 wt.% albumin, respectively. Each porous ceramic achieved a well-developed, interconnected, tri-modal hierarchical microstructure with wide pore size distribution. Larger pore size in the range 250 to 500 μm were achieved, which can be attributed to the relatively higher relative bubble sizes shown in Fig. 8. As the albumin content increased, the size of the interconnection pore decreased, and the sintered body became denser. This densification is expected to increase the mechanical behavior of porous ceramics. Highly interconnected grains can be observed in the higher resolution images in the insert in every microstructure image with

different weight percent. Upon increasing the albumin content, the porous ceramics thus achieved shows higher connectivity, and the sample with 10 wt.% of albumin content was found to be easy to handle, while those with 5 wt.% or less broke easily. So the porous ceramics thus found with albumin content of 10 wt.% was found to be appropriate for the manufacture of a higher amount of porous ceramics for many applications.

Conclusions

Porous SiC ceramics showed open and interconnected microstructure with the pore size of 250 to 500 μm . The viscosity of the slurry varying on the albumin content was found to be typical, as on increasing the wt.% of albumin content, the slurry showed shear thickening behavior. The viscosity of the slurry was found to increase, hindering thick strutting. This gave a more stable wet foam on mechanical frothing that on sintering provided porous ceramics. In terms of the rheological properties, the wet foam was characterized as a function of air content, wet foam stability, bubble size, and relative bubble size. Controlling the air content inside the foam improved the wet foam stability of the wet foam from (20 to 90) % with the increment of albumin content. Proof of the stability was demonstrated by the controlled increment of the relative bubble size to less than 2.5 times. With all these improved parameters upon sintering, highly porous open pore ceramics was achieved for various applications.

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